

III.A.13 SOFC Cathode Materials Development at PNNL

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Objectives

- Develop solid oxide fuel cell (SOFC) cathode materials and microstructures offering low polarization losses and long-term stability at intermediate SOFC operating temperatures (650-800°C).
- Improve understanding of mechanisms affecting cathode performance, including both intrinsic factors (e.g., composition, microstructure) and extrinsic factors (e.g., Cr poisoning).

Approach

- Synthesize, process, and characterize candidate SOFC cathode compositions.
- Utilize carefully controlled SOFC testing to quantify performance of SOFC cathode materials on anode-supported cells.
- Evaluate effects of various interconnect alloys and Cr sources on cathode performance.

Accomplishments

- Developed an improved button cell test fixture design. Evaluated effects of alloy interconnect materials on cathode performance.
- Evaluated effects of Cr vapor species on cathode performance.

Future Directions

- Complete investigation into effects of alloy oxide scale composition on cathode performance.
- Investigate effects of cathode/contact layer chemistry and microstructure on Cr poisoning.
- Improve understanding of cathode “burn-in” phenomenon during initial cell operation.

Introduction

Minimization of electrode polarization processes (especially cathodic polarization) represents one of the greatest challenges to be overcome in obtaining high, stable power densities from SOFCs. Cathodic polarization exhibits a high activation energy relative to the other internal power losses (e.g., electrolyte ohmic losses), so the need to improve cathode performance becomes increasingly important as the targeted SOFC operating temperature is reduced. The severe environmental conditions experienced by the cathode during operation greatly reduce the

number of likely candidate materials. In particular, the cathode material must be stable at the SOFC operating temperature in air, and it must have high electronic conductivity, high catalytic activity for oxygen molecule dissociation and oxygen reduction, and a thermal expansion compatible with the SOFC electrolyte (usually yttria-stabilized zirconia, YSZ). Chemical interactions with the electrolyte and interconnect materials must be minimal. In addition, the cathode material must have a porous microstructure so that gaseous oxygen can readily diffuse through the cathode to the cathode/electrolyte interface. This porous morphology must remain

unchanged during SOFC operation over the lifetime of the cell.

For high-temperature SOFCs operating at around 1000°C, the preferred cathode material is Sr-doped lanthanum manganite, LSM, which offers adequate electrical conductivity and electrocatalytic activity, reasonable thermal expansion, and stability in the SOFC cathode operating environment. For SOFCs operating at substantially lower temperatures, such as 650-800°C, alternative cathode materials may be required, since lanthanum manganite does not appear to be a satisfactory choice due (at least in part) to its low ionic conductivity and slow surface oxygen exchange kinetics. Alternative perovskite compositions—typically containing La on the A site and transition metals such as Co, Fe, and/or Ni on the B site—have received attention. In general, they offer higher oxygen ion diffusion rates and exhibit faster oxygen reduction kinetics at the electrode/electrolyte interface than lanthanum manganite. In recent years, Pacific Northwest National Laboratory (PNNL) has developed an optimized Sr-doped lanthanum ferrite (LSF) cathode which delivers high power density in anode-supported cells ($\sim 1.2 \text{ W/cm}^2$ at 800°C and $\sim 0.8 \text{ W/cm}^2$ on button cells at 750°C; measured at 0.7 V; fuel is 97% H_2 /3% H_2O ; oxidant is air; low fuel and air utilization). In recent work at PNNL, interactions between candidate SOFC cathode materials (LSM and LSF) and a state-of-the-art interconnect alloy (Crofer22APU) were evaluated using single-cell electrochemical testing, x-ray diffraction (XRD), and scanning electron microscopy/energy dispersive x-ray (SEM/EDS). The effects of Cr vapor species on these cathode materials were also investigated.

Approach

Cathode powders were synthesized using the glycine-nitrate combustion technique. The powders were processed to obtain the desired particle size distribution, and then applied to anode-supported YSZ membranes with a samarium-doped ceria (SDC) interlayer. The resulting cells were placed into test fixtures, and current-voltage data were recorded from 700-850°C. For long-term tests, the cells were held at 0.7 V and periodically subjected to current sweeps from 0-7 A. A mixture of 97% H_2 -3% H_2O was flowed to the anode at 200 sccm, and

air to the cathode at 300 sccm. For alloy interaction tests, alloy current collectors were used on the cathode side (tests were also performed with Pt current collectors to provide an idealized performance baseline). After cell tests were completed, the cells were analyzed by SEM/EDS. Cathode material/alloy interactions were also studied using high-temperature XRD (HTXRD).

Results

Significant degradation of performance was observed when a commercial SOFC interconnect alloy (Crofer22APU) was used as the cathode current collector in a newly designed button cell fixture. (The primary advantage of this new test fixture over conventional button cell fixtures lies in the fact that it does not depend on expensive (and unrealistic) sintered platinum cathode current collectors. Instead, it utilizes actual candidate current collector materials for SOFC stacks, thereby providing a means of assessing interactions between interconnect, contact, and cathode materials). Degradation was not observed when Pt was used as the current collector. Potential sources of degradation include solid-state reaction of the alloy oxide scale (Cr_2O_3 and $(\text{Mn,Cr})_3\text{O}_4$ spinel) with the cathode material, and reaction of volatile Cr species with the cathode material. While both cathode materials showed a significant decrease in performance over a relatively limited period of operation, the mechanisms of the degradation appear to vary from one cathode material to another.

LSF Cathode. Figure 1 indicates cell performance data utilizing an LSF-20 cathode with a Crofer cathode current collector at 750°C and 0.7 V. The data is compared to a similar cell with a Pt current collector. The Crofer-containing cell indicated rapid degradation in performance, whereas the sample utilizing the Pt current collector showed typical performance characteristics for LSF-based cells (cell conditioning over 100-200 hours followed by stable performance). SEM/EDS analysis of the tested cathode revealed Cr distributed throughout the LSF cathode and also in the SDC interlayer. HTXRD of an LSF-20 film on Crofer foil during heating in air at 800°C for 72 hours indicated the formation of a high Fe-containing oxide ($\text{SrFe}_{12}\text{O}_{19}$). These results suggest that the Cr diffuses into the

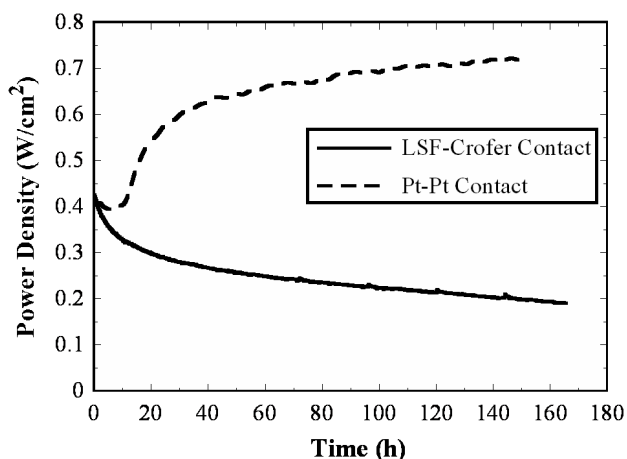


Figure 1. Test Results for Cells with LSF Cathode

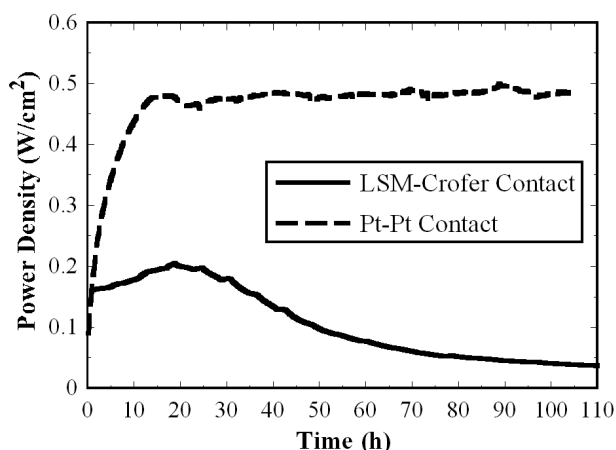


Figure 2. Test Results for Cells with LSM Cathode

LSF perovskite, where it presumably displaces Fe cations on B sites in the ABO_3 lattice structure.

LSM Cathode. Figure 2 indicates cell performance data for LSM/Crofer and LSM/Pt cells; again, there was significant disparity between the two samples. Without the Crofer alloy, LSM indicated a typical conditioning effect followed by stable performance of ~ 500 mW/cm². When Crofer was utilized as the cathode current collector, an initial “burn-in” was also observed, but within 20 hours of testing the cell began to severely degrade. SEM/EDS analysis of the tested cathode revealed no discernible Cr within the LSM cathode, but within the SDC-20 interlayer, as much as 5 atomic % Cr was detected. HTXRD indicated no discernible reaction products between the Crofer foil and LSM cathode

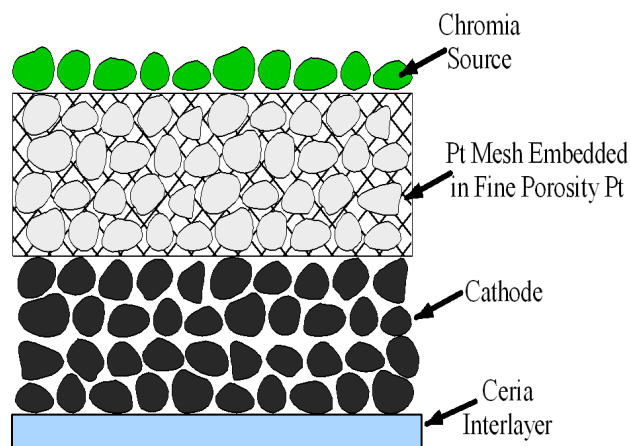


Figure 3. Schematic Illustration of Test Configuration for Cr Vapor Tests

even after 120 hours at 800°C. Adjacent to the Crofer wire, approximately 1-2 atomic % Cr was apparent, and SEM did indicate a segregated high Cr phase (possibly $SrCrO_4$).

Cr Vapor Tests. Tests evaluating the effect of Cr vapor species on cathode performance were performed by physically separating the Cr vapor source (Cr_2O_3 , $MnCr_2O_4$, or Sr-doped lanthanum chromite) from the cathode (test configuration shown schematically in Figure 3). Preliminary results found that degradation rates were dependent on the Cr source ($Cr_2O_3 > MnCr_2O_4 > Sr$ -doped lanthanum chromite). It is believed that this trend in degradation rate correlates with the Cr volatilization rate for each source. Cr_2O_3 is known to exhibit higher Cr volatilization rates than lanthanum chromite, and tentative calculations indicate that $MnCr_2O_4$ has a volatilization rate intermediate between the other oxides.

Conclusions

The performance of LSM and LSF cathodes at intermediate temperatures can be affected by the presence of Cr-containing materials (alloys and oxides). Both solid-state and vapor-phase interactions have been observed for cells tested with a commercial Cr-containing interconnect alloy. Studies are in progress to more fully ascertain the conditions under which performance degradation occurs and the specific mechanisms which lead to degradation.

FY 2004 Publications/Presentations

1. M.D. Anderson, J.W. Stevenson and S.P. Simner, "Reactivity of Lanthanide Ferrite SOFC Cathodes with YSZ Electrolyte," *Journal of Power Sources*, **129** [2] (2004) 188.
2. S.P. Simner, M.D. Anderson and J.W. Stevenson, "La(Sr)FeO₃ Cathodes with Marginal Cu Doping," *J. Am. Ceram. Soc.*, in press (2004).
3. S.P. Simner, J.F. Bonnett, M.D. Anderson and J.W. Stevenson, "Low Temperature Sinterability of La(Sr)FeO₃ Cathodes on YSZ," *Solid State Ionics*, in press (2004).
4. S.P. Simner, J.F. Bonnett, M.D. Anderson and J.W. Stevenson, "Enhanced Low Temperature Sintering of (Sr, Cu) Doped Lanthanum Ferrite Cathodes," *Solid State Ionics*, in press (2004).
5. S.P. Simner, M.D. Anderson and J.W. Stevenson, "Development of Anode-Supported SOFCs and Low Temperature Cathodes," 2003 Fuel Cell Seminar, Miami Beach, Florida, November 3-7, 2003.
6. S.P. Simner, J.F. Bonnett, M.D. Anderson and J.W. Stevenson, "Lanthanum Ferrite Cathode Development at PNNL," 2003 ASM Materials Solutions Conference and Exposition, Pittsburgh, Pennsylvania, October 13-15, 2003.